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Abstract

The invention concerns a composite ion exchange membrane based on the microporous polypropylene film and preparation method thereof. The ion
5 exchange membrane possesses excellent electrochemical, mechanical and chemical stabilities. Tensile strength is 60-90 Mpa, folding angle is typically 0° , surface resistance is generally less than $5 \Omega \cdot \text{cm}^2$ (0.5 N, aqueous NaCl solution), and selective static migration constant of ion is generally more than 0.85 (0.5 N/1.0 N NaCl solution), and aqueous swellability is 0-5%. In addition,
10 it is acid-resistant and alkali-resistant. The ion exchange composite membrane may be obtained by polymerizing microporous polypropylene film with monomer having or able to introduce ion exchange groups and proper treatment. It may be used in separating process such as desalting-purification, concentration, diffusive dialysis, pressure filtration, pervaporation and the like,
15 electrochemical preparation and fuel battery.

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[54]发明名称 聚丙烯微孔膜为基膜的高分子交换膜及其制法

[57]摘要

本发明涉及一种以聚丙烯微孔膜为基膜的复合型离子交换膜及其制法。这种复合膜兼有优良的电学、力学和化学稳定性能，拉伸强度为 60—150MPa，可折叠角一般为 0°，面电阻一般小于 5Ω·cm²(0.5N NaCl 水溶液)，选择透过离子的扩散迁移数一般大于 0.85(0.5N 1.0N NaCl 水溶液)，水中溶胀度为 0—5%，耐酸、碱。该膜可用聚丙烯微孔膜含浸带有或可引入离子交换基团的单体后聚合、处理得到。该膜可用于脱盐纯化、浓缩、扩散渗析、压渗析、渗透蒸发等分离过程和电化学制备过程以及燃料电池中。

权 利 要 求 书

1、一种聚丙烯微孔膜为基膜的离子交换膜，其特征在于：

(1) 由厚度为 $15-50\mu\text{m}$ 的双轴拉伸聚丙烯微孔膜为基膜和复合在基膜上的离子交换树脂构成，所复合的离子交换树脂带有或引入了强酸性或弱酸性阳离子交换基团，或者强碱性或弱碱性阴离子交换基团；

(2) 力学性能和力学均匀性：

在膜面内各方向的拉伸强度为 $60-150\text{MPa}$ ，断裂伸长率大于 20% ，最大为 $150-200\%$ ，杨氏模量为 $1.0-3.0\text{GPa}$ ，可折叠角度 $0-45^\circ$ ；

(3) 离子交换树脂复合量：膜的复合量为 $20-70\%$ ，膜的离子交换容量为 $1.5-7.0\text{meq/g}$ 。

(4) 膜的导电性和离子透过选择性：膜的面电阻为 $0.01-20\Omega\cdot\text{cm}^2$ ，选择透过离子的静态迁移数为 $0.80-0.99$ ；

(5) 膜的耐酸碱性和耐溶胀性：在水中的溶胀度为 $0-5\%$ 。

2、根据权利要求1所述的一种聚丙烯微孔膜为基膜的离子交换膜，其特征在于膜的复合量为 $30-70\%$ ，面电阻为 $0.01-5\Omega\cdot\text{cm}^2$ ，选择透过离子的静态迁移数为 $0.85-0.99$ ，可折叠角度为 0° 。

3、一种聚丙烯微孔膜为基膜的离子交换膜的制法，其特征在于工艺路线可采用一步法或两步法：

a. 一步法，是将一种或多种带有离子交换基团的单体与其它助剂配制成混合溶液，再将聚丙烯微孔膜在混合液中浸渍，然后将微孔膜中吸入的单体进行聚合反应而得到离子交换膜，该膜经洗涤后即成品；

b. 两步法，是(1)将一种或多种可引入离子交换基团的单体和其它助剂配制成混合溶液，再将聚丙烯微孔膜在混合液中浸渍，然后使微孔膜中的单体进行聚合反应而得到原始型复合膜；(2)在原始型复合膜中引入离子交换基团，使其转化为离子交换膜，膜经洗涤后即成为成品。

4、根据权利要求3所述的离子交换膜的制法，其特征在于所述的带有或可引入离子交换基团的单体为加成聚合型的或缩合聚合型的，它们的聚合反应是加成聚合反应或缩合聚合反应，聚合方法包括引发剂引发聚合，热引发聚合，紫外光或 γ 射线辐照引发聚合。

5、如权利要求3，4所述的离子交换膜的制法，其特征在于所说带有或可引入离子交换基团的单体为苯乙烯、对苯乙烯磺酸酯、氯甲基苯乙烯、对氨基苯乙烯、对甲氨基苯乙烯、对二甲氨基苯乙烯、乙烯基吡啶、2-甲基-5-乙烯基吡啶、丙烯酸、丙烯酸甲酯、丙烯酸乙酯、丙烯酸丁酯、丙烯酸缩水甘油酯、甲基丙烯酸、甲基丙烯酸缩水甘油酯，或上述一种或数种的混合物；所说的带有或可引入离子交换基团的缩合聚合型单体可以是苯酚磺酸、对羟基苯基磺酸、水杨酸、苯胺、间苯二胺、乙二胺、二乙撑三胺、四乙撑五胺、对甲基苯磺酸、蜜胺、碳酸胍、二氰胺、乙烯亚胺、二甲基(4-羟代苄基)胺、间甲苯胺与甲醛、多聚甲醛、乙二醛、糠醛及丙酮，配制混合液时单体的含量为30—100%。

6、根据权利要求3所述的离子交换膜的制法，其特征在于所述的助剂为引发剂、交联剂、增韧剂、增塑剂、无机或有机溶剂；其中引发剂为通用的偶氮二异丁腈、过氧化苯甲酰，其用量为混合液

的0-5%；交联剂为二乙烯苯、丁二烯、双甲基丙烯酸乙二醇酯、双甲基丙烯酸缩二乙二醇酯、双甲基丙烯酸二缩三乙二醇酯、二乙烯基醚、苯酚、甲酚、间苯二酚，交联剂在混合液中的含量为0-40%；增韧剂为丁二烯、苯乙烯，增韧剂在混合液中的含量为0-40%，增塑剂为邻苯二甲酸二辛酯、邻苯二甲酸二丁酯、磷酸三苯酯，增塑剂在混合液中的含量为0-30%；无机或有机溶剂为水、四氯化碳、四氯乙烯、二氯乙烷，其含量为0-20%。

7、根据权利要求3所述的离子交换膜的制法，其特征在于聚丙烯微孔膜在混合液中浸渍的温度为0-50℃，浸渍时间为0.1-24小时。

8、根据权利要求3所述的离子交换膜的制法，其特征在于含浸单体进行聚合反应的条件：反应温度为50-100℃，反应时间为30分钟至24小时。

9、根据权利要求3所述的离子交换膜的制法，其特征在于引入离子交换基团的方法：将原始复合膜水解、磺化、或氯甲基化和胺化；通过磺化引入酸性离子交换基团时，磺化剂可为浓硫酸、氯磺酸、硫酸氯、发烟硫酸、三氧化硫、磺化温度为20-70℃。

10、根据权利要求3所述的离子交换膜的制法，其特征在于膜的洗涤可为酸洗、碱洗、盐液洗涤、有机溶剂洗涤或水洗。

说 明 书

聚丙烯微孔膜为基膜的离子交换膜及其制法

本发明涉及一种聚丙烯微孔膜为基膜的复合型离子交换膜及其制备方法。

离子交换膜具有非常广泛的用途，在以电渗析为基础的脱盐纯化、浓缩分离、反应制备过程中以及扩散渗析，压渗析等方面的应用都达到了相当高的工业化水平。对离子交换膜的基本性能要求包括高的导电性和离子透过选择性、优良的力学性能(机械强度、柔韧性和形态稳定性)和化学稳定性。这些性能要求经常是互相制约的，因此制备综合性能优良的离子交换膜一直受到广泛重视。完全由离子交换树脂制成的膜可以有很好的电化学性能，但力学性能很差，因而难以作为离子交换膜在实际中应用。一般都采用离子交换树脂与其它材料复合的办法。例如可用将离子交换树脂和其它高分子共混的方法制备成复合膜。在实际中也常用一些多孔材料，如玻璃纤维布、合成纤维布、高分子多孔膜等为基膜，然后将离子交换树脂引入基膜制得复合型离子交换膜。由于这些基膜中的孔洞尺寸较大，例如数十或数百微米以上，因此膜的局部力学性能仍不理想。曾有报导采用Celgard牌号聚丙烯微孔膜为基膜制备复合型离子交换膜[日本公开特许公报，昭51--103089和B. Glad and K. Irgum, J. Membrane Sci., 67, 289(1992)]。这种基膜中微孔尺寸一般在微米以下，但它的力学性能均匀性差，横向强度极差，在水溶液中横向方向仍有较大的溶胀(>10%)，离子透过选择性不高。

本发明的目的是针对已有技术的缺点发展综合性能优越的新的复合型离子交换膜和它的制备方法。

本发明的离子交换膜由基膜和复合在基膜上的交联聚电解质(离子交换树脂)构成。本发明采用双轴拉伸法制备的高性能聚丙烯微孔膜(见中国专利CN 1017682B)为基膜进行复合, 它兼有优良的力学性能和气体透过性。微孔膜在膜面内各方向的拉伸强度为60—150MPa, 孔隙率一般为20—60%(体积分数), 最好应在30%以上, 以确保高的复合量。微孔孔径一般为0.001—10 μ m, 大部分分布在0.005—1 μ m之间, 孔径太小则导电性下降, 孔径太大则力学性能和离子透过选择性下降。孔的尺寸均匀性要高, 以避免龟裂, 保证力学性能良好。微孔膜厚度可根据需要选用, 一般为15—50 μ m。

本发明所复合的离子交换树脂可以是强酸性或弱酸性阳离子交换树脂和强碱性或弱碱性阴离子交换树脂。复合量为20—70%(重量), 最好在30%以上。离子交换膜的离子交换容量为1.5—7.0meq/g。

本发明的离子交换膜有很高的导电性和离子透过选择性, 膜的面电阻在0.01—20 Ω .cm²范围内(0.5N NaCl水溶液), 一般小于5 Ω .cm²; 选择透过离子的静态迁移数在0.80—0.99之间(0.5N NaCl/1.0N NaCl水溶液), 一般大于0.85。

本发明的离子交换膜有优良的力学性能。膜面内力学性能均匀, 室温条件下拉伸强度一般可达60MPa, 最大可达150MPa; 断裂伸长一般不低于20%, 最大可达150—200%; 杨氏模量为1.0—3.0GPa; 可折叠角度不大于45°, 一般为0°。

本发明的离子交换膜在水溶液中膜面方向的耐溶胀性能优良，溶胀度为0—5%，一般小于3.0%。由于采用聚丙烯材质的基膜，因此本发明的离子交换膜耐酸、碱性能优良。

本发明建议的复合型离子交换膜的制备工艺包括一步法和两步法两种。

一步法的工艺路线是：

(1) 将一种或多种带有离子交换基团的单体与其它助剂配成混合溶液。

(2) 将聚丙烯微孔膜在混合液中浸渍。

(3) 将微孔膜中的单体聚合得到离子交换膜，经洗涤后该膜即可使用。

两步法的工艺路线是：

(1) 将一种或多种可引入离子交换基团的单体和其它助剂配成混合液。

(2) 将聚丙烯微孔膜在混合液中浸渍。

(3) 将微孔膜中的单体聚合得到原始型复合膜。

(4) 在原始型复合膜中引入离子交换基团，使之转化为离子交换膜，该膜经洗涤后即可使用。

本发明制备方法中，带有或可引入离子交换基团的单体可以是加成聚合型(简称聚合型)或缩合聚合型(简称缩聚型)。聚合反应的类别可相应是加成聚合(包括共聚合)和缩合聚合(包括共缩聚)。聚合方法可以是加入引发剂引发聚合，也可以是热引发聚合，紫外光

或 γ 射线辐照引发聚合。

本发明所用的带有或可引入离子交换基团的单体可以是苯乙烯、对苯乙烯磺酸酯、氯甲基苯乙烯、对胺基苯乙烯、对甲胺基苯乙烯、对二甲胺基苯乙烯、乙烯基吡啶、2-甲基-5-乙烯基吡啶、丙烯酸、丙烯酸甲酯、丙烯酸乙酯、丙烯酸丁酯、丙烯酸缩水甘油酯、甲基丙烯酸、甲基丙烯酸缩水甘油酯。本发明所用带有或可引入离子交换基团的缩合型单体可以是苯酚磺酸、对羟基苄基磺酸、水杨酸、苯胺、间苯二胺、乙二胺、二乙撑三胺、四乙撑五胺、对甲基苯磺酸、蜜胺、碳酸胍、二氰胺、乙烯亚胺、二甲基(4-羟代苄基)胺、间甲苯胺与甲醛、多聚甲醛、乙二醛、糠醛和丙酮。

本发明中配制单体混合液时所用的助剂可以是引发剂、交联剂、增韧剂、增塑剂、无机或有机溶剂中的一种或几种。引发剂为通用引发剂，可以是偶氮类如偶氮二异丁腈、过氧化物类如过氧化苯甲酰。混合液中引发剂的重量含量视单体种类而定，一般在0—5%之间，太多会影响复合离子交换膜的性能，太少会使聚合时间延长。交联剂可以是二乙烯苯、丁二烯、双甲基丙烯酸乙二醇酯、双甲基丙烯酸缩二乙二醇酯、双甲基丙烯酸二缩三乙二醇酯、二乙烯基醚、苯酚、甲酚、间苯二酚。混合液中交联剂的含量(重量)在0—40%之间，太多会降低膜的柔韧性和导电性。增韧剂可以是丁二烯、苯乙烯，在混合液中含量(重量)在0—40%之间，以保证离子交换膜良好的力学性能。增塑剂为通用增塑剂，可以是邻苯二甲酸二辛酯、邻苯二甲酸二丁酯、磷酸三苯酯，在混合液中的含量(重量)为0—

30%，以保证原始型复合膜和离子交换膜良好的力学性能和可加工性。无机或有机溶剂为通用溶剂，可以是水、四氯化碳、四氯乙烯、二氯乙烷，以调节混合液的粘度及混合液的均一性，含量(重量)在0—20%之间。

本发明中浸渍聚丙烯微孔膜的混合液中，带有或可引入离子交换基团的单体的含量(重量)为30—100%。含量太低，会使所制得膜的电化学性能下降。

聚丙烯微孔膜在混合液中浸渍的温度和时间随单体及助剂的种类而异，一般在0—50℃，浸渍时间为0.1—24小时。为使单体溶液易于被均匀地含浸在基膜的微孔中，也可用表面处理的方法使基膜材料表面具有亲水性。

本发明中聚合反应的温度、压力等条件随单体及助剂的种类而异，一般在低于100℃下反应，较好温度范围是50—100℃，时间在30分钟—24小时之间。

本发明中引入离子交换基团的方法可以在酸或碱性溶液中水解、磺化、氯甲基化、胺化。通过磺化引入酸性离子交换基团时，磺化剂可以是浓硫酸、氯磺酸、硫酰氯、发烟硫酸、三氧化硫。磺化温度和时间随磺化剂及磺化剂浓度不同而定。一般在90℃以下，以20—70℃为佳。

本发明中膜的洗涤可以是酸洗、碱洗、盐液洗涤、有机溶剂洗涤、水洗。

本发明所制得的离子交换膜具有良好的综合性能，导电性高、

离子透过选择性高、耐溶剂溶胀、力学性能优良、化学稳定性好。制备方法简便易行，可大规模生产。本发明具有极大的应用前景，可望用于脱盐纯化、浓缩分离、扩散渗析、压渗析、渗透蒸发等分离过程和置换、水解、复分解等电化学制备过程以及燃料电池中。

实施例1

79份丙烯酸与10份二乙烯苯、9份蒸馏水、2份过氧化苯甲酰配成混合液；将孔隙率36%，平均孔径 $0.05\mu\text{m}$ ，厚度 $30\mu\text{m}$ ，双轴拉伸的聚丙烯微孔膜含浸此液， 70°C 下，聚合4小时，得到弱酸性阳离子交换膜，膜的交换容量为 5.20meq/g ，面电阻为 $1.8\Omega\cdot\text{cm}^2$ (0.5N NaCl 水溶液中)，钠离子的静态迁移数为0.96 ($0.5\text{N}/1.0\text{N NaCl}$ 水溶液)，可折叠角为 0° ，杨氏模量为 2.70GPa ，拉伸强度为 75MPa ，断裂伸长率40%，纯水中膜面方向的溶胀度小于1.5%。

实施例2

97份丙烯酸丁酯和2份二乙烯苯、1份过氧化苯甲酰配成混合溶液，用与实施例1相同的聚丙烯微孔膜含浸此液30分钟， 70°C 下聚合16小时；将原始复合膜在 70°C 、8.0%的氢氧化钠/乙醇溶液中水解72小时，水洗。所得弱酸性阳离子交换膜的交换容量为 5.95meq/g ，面电阻为 $2.0\Omega\cdot\text{cm}^2$ ，钠离子迁移数为0.92，可折叠角为 0° ，杨氏模量为 2.50GPa ，拉伸强度为 72MPa ，断裂伸长率为46%，纯水中膜面方向上的溶胀度小于3.0%。

实施例3

88份丙烯酸丁酯、10份二乙烯苯、2份过氧化苯甲酰配成混合溶

液，用同实施例2的聚丙烯微孔膜含浸此液，用同实施例2的方法制备弱酸性阳离子交换膜。所得膜的交换容量为5.9meq/g，面电阻为 $2.0\Omega\cdot\text{cm}^2$ ，钠离子静态迁移数为0.96，可折叠角为 0° ，杨氏模量为2.56GPa，拉伸强度为80MPa，断裂伸长率为44%，纯水中膜面方向上的溶胀度小于1.5%。

实施例4

74份苯乙烯，10份二乙烯苯、14份邻苯二甲酸二辛酯，2份过氧化苯甲酰配成混合溶液，用同实施例2的方法制得原始型复合膜，室温下用氯磺酸/二氯乙烷溶液(1:4)磺化40分钟，二氯乙烷、醋酸洗涤。所得强酸性阳离子交换膜的交换容量为3.4meq/g，面电阻为 $1.3\Omega\cdot\text{cm}^2$ ，钠离子静态迁移数为0.98，可折叠角为 40° ，拉伸强度为72MPa，断裂伸长率为25%，杨氏模量为2.70GPa，纯水中膜面方向上的溶胀度小于3.6%。

实施例5

51份苯乙烯，24份丙烯酸丁酯、14份邻苯二甲酸二辛酯，10份二乙烯苯、1份过氧化苯甲酰配成混合溶液，用同实施例4的方法制备强酸性阳离子交换膜。膜的交换容量为3.47meq/g，面电阻为 $3.0\Omega\cdot\text{cm}^2$ ，钠离子静态迁移数为0.94，可折叠角为 10° ，杨氏模量为2.60GPa，纯水中膜面方向上的溶胀度小于2.5%。

实施例6

用与实施例2相同的混合液和方法制备原始复合膜，用氯甲醚/二氯乙烷溶液氯甲基化，用饱和三甲胺/乙醇溶液胺化，乙醇、食

盐溶液洗涤，所制得强碱性阴离子交换膜的交换容量为3.30meq/g，面电阻为 $1.5\Omega\cdot\text{cm}^2$ ，氯离子静态迁移数为0.97，可折叠角为 40° ，杨氏模量为2.80GPa，拉伸强度为80MPa，断裂伸长率为40%，纯水中膜面方向上的溶胀度小于1.2%。

实施例7

用丙烯酸缩水甘油酯99份，二乙烯苯0.5份，过氧化苯甲酰0.5份，配成混合溶液，用同实施例2的方法制备原始型复合膜，用25%三甲胺水溶液胺化，所制得强碱性阴离子交换膜的交换容量为3.18meq/g，面电阻为 $3.2\Omega\cdot\text{cm}^2$ ，氯离子静态迁移数为0.96，可折叠角为 0° ，杨氏模量为2.80GPa，拉伸强度为78MPa，断裂伸长率为60%，纯水中膜面方向上的溶胀度小于0.5%。

Description

An Ion exchange Membrane Based on the Microporous Polypropene Film and Preparation Method thereof

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The invention concerns a composite ion exchange membrane based on the microporous polypropylene film and preparation method thereof.

10 Ion exchange membrane is broadly applied in industry, and particularly in desalting-purification, concentrating-separation, reaction preparation based on electrodialysis, diffusive dialysis, pressure filtration and the like, which has achieving a quite high level. The basic requirements on property of ion exchange membrane include high conductivity and selective permeation of ion, excellent mechanical properties (mechanical strength, flexibility and morphological stability) and chemical stability. The requirements of these properties are always mutual restraint, and therefore the preparation of ion exchange membrane with good combined properties has received wide attention. The ion exchange membrane prepared solely with ion exchange resin may have excellent electrochemical property, but its mechanics property is poor, which makes it difficult to use it in practice. A method combining ion exchange resin and other materials is generally used. For example, a method crossblending ion exchange resin and other polymer is used to prepare composite membrane. In practice, some microporous material such as glass fibre cloth, synthetic fiber cloth, macromolecule porous membrane is often used as basal lamina, into which ion exchange resin is then introduced to make composite ion exchange membrane. Because the pore size of these basal lamina are relatively large, for example, up to several ten to several hundred micrometers, the local mechanical property of the membrane is still undesired. It has been reported that a composite ion exchange membrane is prepared by using microporous polypropene film under the name of Celgard® as basal lamina[JP-A No. sho 51-103089, B. Glad and K. Irgum, J. Membrane Sci., 67,

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289 (1992)]. This ion exchange membrane has a typical pore size less than 1 micrometer, but its mechanical property is poor in uniformity, and particularly in transverse strength. In addition, it has a relatively large degree of swelling (>10%) in landscape orientation in aqueous solution, and low permeation selectivity for ions.

Therefore an object of the present invention is to provide a new composite ion exchange membrane with good combined properties developed by overcoming disadvantages existing in prior art, and preparation method thereof

The ion exchange membrane according to the present invention is consisted of a basal lamina and crosslinking polyelectrolyte (ion exchange resin) combined thereon. In present invention, a microporous polypropylene film with high performance in both mechanical property and air permeability prepared by biaxial stretching method (see Chinese Patent CN 1017682B) is used as basal lamina to perform combination. To ensure a high compound quantity, the tensile strength in each direction of microporous film is 60-150 Mpa, and the porosity is typically 20-60%(volume percentage), preferably more than 30%. The pore size is generally 0.001-10 μm , and mostly distributed in 0.005-1 μm . A small pore size will result in a decrease of electrical conductivity, while a large pore size causes both mechanical property and permeation selectivity for ion decreasing. The uniformity of pore size should be high in order to avoid cracking and ensure a good mechanical property. The thickness of microporous film varies depending on demand and is normally between 15 μm and 50 μm .

The composite ion exchange resin according to the present invention may be strong or weak acid type cation exchange resin or strong or weak alkali type anion exchange resin. The compound quantity is 20-70% by weight, preferably more than 30% by weight. The ion exchange capacity of the ionexchange membrane is 1.5-7.0 meq/g.

The ion exchange membrane according to the present invention is high in electrical conductivity and permeation selectivity for ion, wherein the surface

resistance is in the range of $0.01-20\Omega\cdot\text{cm}^2$ (0.5N, aqueous NaCl solution), generally less than $5\Omega\cdot\text{cm}^2$, and the static migration constant of perm-selective ion is between 0.80 and 0.99 (0.5N NaCl/1.0 N NaCl aqueous solution), typically more than 0.85.

5 The ion exchange membrane according to the present invention possesses a good mechanical property, wherein mechanical property in the membrane is uniform and the tensile strength at room temperature is normally up to 60Mpa, upmost to 150Mpa; the elongation at break is typically no less than 20%, upmost to 150-200%; Young's modulus is 1.0-3.0Gpa; and the folding angle is
10 at most 45° , typically 0° .

The ion exchange membrane according to the present invention is good in swelling resistance in aqueous solution, and the degree of swelling is 0-5%, typically less than 3.0%. Because polypropylene material is applied as basal lamina, the ion exchange membrane according to the present invention is
15 therefore excellent in acid/alkali resistance.

The preparation process of the composite ion exchange membrane according to the present invention includes an one-step method and a two-step method.

The process of one-step method is described as the following:

- 20 (1) Mixing one or more kinds of monomer with ion-exchange group and other accessory ingredients to form a mixed solution,
(2) Dipping a microporous polypropylene film in the mixed solution,
(3) An ion exchange membrane is obtained by polymerizing the monomers in the microporous film, and the resulting membrane can be used
25 after washing.

The process of two-step method is described as follow:

- (1) Mixing one or more kinds of monomer able to introduce ion exchange groups, and other accessory ingredients to form a mixed solution,
(2) Dipping a microporous polypropylene film in the mixed solution,
30 (3) Original type composite membrane is obtained by polymerizing the

monomers in the microporous film,

(4) An ion exchange membrane is obtained by introducing ion exchange groups into the original type composite membrane, and the resulting membrane can be used after washing.

5 In the preparation method according to the present invention, the monomers having or able to introduce ion exchange groups may be addition polymerization type (for short addition type) or condensation polymerization type (for short condensation type). Correspondingly the type of polymerization may be addition polymerization (including co-polymerization) and
10 condensation polymerization (including co-polycondensation). The polymerization method comprises polymerization with initiator, polymerization initiated with thermo, polymerization initiated with UV ray or polymerization initiated with radiating of γ -ray.

The monomers having or able to introduce ion exchange groups according
15 to the present invention may be selected from the group consisting of styrene, *p*-styrene sulfonate, chloromethyl styrene, *p*-aminostyrene, *p*-methylanino styrene, *p*-dimethylanino styrene, vinyl pyridine, 2-methyl-5-vinyl pyridine, acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, glycidyl acrylate, methylacrylic acid, glycidyl methylacrylate. The condensed type monomer
20 having or able to introduce ion exchange groups used in the present invention may be selected from the group consisting of sulfocarbolic acid, *p*-hydroxybenzylsulfonic acid, *o*-hydroxybenzoic acid, aniline, *m*-phenylenediamine, ethylenediamine, diethylene triamine, tetraethylene peatamine, *p*-methyl phenylsulfonic acid, melamine, guanidine carbonate,
25 dicyandiamide, ethyleneimine, dimethyl(4-hydroxybenzyl)amine, *m*-methyl phenethylamine and formaldehyde, polyformaldehyde, ethanedial, furfuraldehyde and acetone.

The accessory ingredients used in the preparation of the mixed solution of monomers according to present invention may be one or more selected from
30 initiator, cross-linking agent, flexibilizer, plasticizer, inorganic or organic

solvent. The initiator is a common initiator, for example azo type initiator such as azodiisobutyronitrile, peroxide type initiator such as benzoperoxide. The amount of initiator used in the mixed solution varies depending on the type of monomer, and is typically in the range of 0-5%. An excess of initiator would
5 influence the property of composite ion exchange membrane while a deficiency of initiator results in the prolongation of polymerization process. The cross-linking agent may be selected from the group consisting of divinylbenzene, butadiene, ethylene glycol dimethylacrylate, diethylene glycol dimethylacrylate, triethylene glycol dimethylacrylate, divinyl ether, phenol,
10 cresol, resorcin. The content(weight) of the cross-linking agent in the mixed solution is between 0% and 40%. An excess of cross-linking agent in the mixed solution would decrease the flexibility and electrical conductivity of the membrane. The flexibilizer used in the present invention may be butadiene, styrene and the amount (weight) thereof in the mixed solution is between 0%
15 and 40% so as to ensure an excellent mechanical property of the ion exchange membrane. The plasticizer used in the present invention may be a common plasticizer such as dioctyl phthalate, dibutyl phthalate, and triphenyl phosphate. The amount (weight) of plasticizer in mixed solution is between 0% and 30% so as to ensure a good mechanical property and machinability of the original
20 type composite membrane and the ion exchange membrane. The inorganic or organic solvent may be a common solvent such as water, carbon tetrachloride, ethylene tetrachloride or dichloroethane and the amount (weight) thereof is between 0% and 20 % so as to adjust the viscosity and homogeneity of the mixed solution.

25 In the present invention, the content (weight) of the monomer having or able to introduce ion exchange group in the mixed solution for dipping microporous polypropylene film is 30-100%. A low content would result in the decrease of electrochemical property of the membrane obtained.

The temperature and time for dipping the microporous polypropylene film
30 in mixed solution varies depending on the types of the monomer and accessory

ingredients. The temperature is generally from 0 °C to 50 °C, and the dipping time is 0.1-2.4 hours. In order to facilitate the uniform distribution of monomer solution dipped in the micropores of basal lamina, a surface treatment method may also be used to confer the the surface of basal lamina material
5 hydrophilicity.

The polymerization conditions such as temperature, pressure and the like in the present invention varies according to the types of the monomer and accessory ingredients. The reaction is usually performed below 100°C, more preferably 50-100°C. The reaction time is between 30 minutes and 24 hours.

10 The method for introducing ion exchange groups in the present invention may be selected from the group consisting of hydrolysis in an acid or alkali solution, sulfonation, chloromethylation, aminization. In the case of introducing an acidic ion exchange group by sulfonation, the sulfonating agent may be selected from concentrated sulphuric acid, chlorosulfonic acid, sulfuric
15 chloride, fuming sulfuric acid or sulfur trioxide. The temperature and time of sulfonation reaction depends on the sulfonating agent and concentration thereof. The sulfonation temperature is typically below 90°C, preferably 20°C - 70°C.

The membrane obtained in the present invention may be washed with acid,
20 alkali, brine, organic solvent or water.

The ion exchange membrane obtained in the present invention has a good combined properties, for example, high electrical conductivity, high permeation selectivity for ion, resistance to solvent swell, excellent mechanical property, and good chemical stability. Further, the preparation method of the
25 ion exchange membrane according to the present invention is easy to practised and suitable for production in a large scale. The present invention is very promising to be used in separating process such as desalting-purification, concentrating-separation, diffusive dialysis, pressure filtration, pervaporation and the like, electrochemical preparation such as displacement, hydrolysis,
30 double decomposition as well as fuel battery.

Example 1

79 parts of acrylic acid, 10 parts of divinyl benzene, 9 parts of distilled water, and 2 parts of benzoperoxid was mixed into a solution. Then the microporous polypropylene membrane stretched in double-axe method with a porosity ratio of 36%, an average pore size of $0.05\mu\text{m}$ and a thickness of $30\mu\text{m}$ was dipped into the mixed solution. A weak acidic cation exchange membrane was obtained after polymerizing for 4 hours at 70°C . The exchange capacity of the resulting membrane was 5.02 meq/g , its surface resistance is $1.8\Omega\cdot\text{cm}^2(0.5\text{N})$, in aqueous NaCl solution, the static migration constant of sodium ion is $0.96(0.5\text{N NaCl}/1.0\text{ N NaCl aqueous solution})$, folding angle is 0° , Young's modulus is 2.70Gpa , tensile strength is 75Mpa , the elongation at break is 40%, and the swell degree along the membrane surface in pure water is less than 1.5%.

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Example 2

97 parts of butyl acrylate, 2 parts of divinyl benzene and 1 part of benzoperoxid was mixed into a solution. Then a microporous polypropylene membrane same as that of example 1 was dipped into the mixed solution for 30 minutes, polymerizing at 70°C for 16 hours. Thereafter the original composite membrane was hydrolyzed at 70°C in ethanol solution containing 8.0% NaOH for 72 hours and washed with water. The exchange capacity of the obtained weak acidic cation ion exchange membrane was 5.95 meq/g , its surface resistance is $2.0\Omega\cdot\text{cm}^2$, the static migration constant of sodium ion is 0.92, folding angle is 0° , Young's modulus is 2.50Gpa , tensile strength is 72Mpa , the elongation at break is 46%, and the swell degree along the membrane surface in pure water is less than 3.0%.

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Example 3

88 parts of butyl acrylate, 10 parts of divinyl benzene and 2 part of

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benzoperoxid was mixed into a solution. Then a microporous polypropylene membrane same as that of example 2 was dipped into the mixed solution and a weak acidic cation ion exchange membrane was obtained by the same method as example 2. The exchange capacity of the obtained membrane was 5.9 meq/g, its surface resistance is $2.0\Omega\cdot\text{cm}^2$, the static migration constant of sodium ion is 0.96, folding angle is 0° , Young's modulus is 2.56Gpa, tensile strength is 80Mpa, the elongation at break is 44%, and the swell degree along the membrane surface in pure water is less than 1.5%.

10 Example 4

74 parts of styrene, 10 parts of divinyl benzene, 14 parts of dioctyl phthalate, and 2 parts of benzoperoxid was mixed into a solution. Then an original composite membrane was prepared in the same manner as in that of example 2. The original membrane was further sulfonated with chlorosulfonic acid/dichloroethane solution (1:4) at room temperature for 40 minutes and then washed with dichloroethane and acetic acid, respectively. The exchange capacity of the obtained strong acidic cation exchange membrane was 3.4 meq/g, its surface resistance is $1.3\Omega\cdot\text{cm}^2$, the static migration constant of sodium ion is 0.98, folding angle is 40° , tensile strength is 72Mpa, the elongation at break is 25%, Young's modulus is 2.70Gpa, and the swell degree along the membrane surface in pure water is less than 3.6%.

Example 5

51 parts of styrene, 24 parts of butyl acrylate, 14 parts of dioctyl phthalate, 10 parts of divinyl benzene, and 1 part of benzoperoxid was mixed into a solution. Subsequently, a strong acidic cation exchange membrane was prepared in the same manner as that of example 4. The exchange capacity of the obtained membrane was 3.47 meq/g, its surface resistance is $3.0\Omega\cdot\text{cm}^2$, the static migration constant of sodium ion is 0.94, folding angle is 10° , Young's modulus is 2.60Gpa, and the swell degree along the membrane surface in pure

water is less than 2.5%.

Example 6

An original composite membrane was prepared with the same mixed
5 solution and method as example 2 and then chloromethylated with
chloromethyl ether/dichloroethane solution, aminated with saturated
trimethylamine/ethanol solution, and washed with ethanol and NaCl solution,
respectively. The exchange capacity of the obtained strong alkalic anionic
exchange membrane was 3.30 meq/g, its surface resistance is $1.5\Omega\cdot\text{cm}^2$, the
10 static migration constant of sodium ion is 0.97, folding angle is 40° , Young's
modulus is 2.80Gpa, tensile strength is 80Mpa, the elongation at break is 40%,
and the swell degree along the membrane surface in pure water is less than
1.2%.

15 Example 7

99 parts of glycial acrylate, 0.5 parts of divinyl benzene, and 0.5 parts of
benzoperoxid was mixed into a solution. An original type composite
membrane was prepared by the same method as example 2 and then aminated
with 25% aqueous trimethylamine solution. The exchange capacity of the
20 obtained strong alkalic anionic exchange membrane was 3.18 meq/g, its
surface resistance is $3.2\Omega\cdot\text{cm}^2$, the static migration constant of sodium ion is
0.96, folding angle is 0° , Young's modulus is 2.80Gpa, tensile strength is
78Mpa, the elongation at break is 60%, and the swell degree along the
membrane surface in pure water is less than 0.5%.

Claims

1. An ion exchange membrane based on the microporous polypropylene film, characterized in that:

5 (1) it is consisted of microporous polypropylene film with a thickness of 15-50 μm prepared by biaxial stretching method and ion exchange resin thereon, said ion exchange resin having or being introduced with strong or weak acidic cation exchange group, or strong or weak alkaline anion exchange group;

10 (2) mechanical property and mechanical homogeneity:

the tensile strength in each direction of membrane surface is 60-150Mpa, the elongation at break is more than 20%, at most 150-200%, Young's modulus is 1.0-3.0Gpa and the folding angle is 0° - 45° ,

(3) compound quantity of ion exchange resin: the compound quantity of 15 the membrane is 20-70%, the ion exchange capacity is 1.5-7.0meq/g,

(4) conductivity and ion permeation selectivity of the membrane:

surface resistance of the membrane is $0.01-20\Omega\cdot\text{cm}^2$, and selective static migration constant of ion is 0.80-0.99;

(5) Acid/alkali resistance and swelling resistance of the membrane:

20 degree of swelling in water is 0-5%.

2. An ion exchange membrane based on the microporous polypropylene film according to claim 1, characterized in that the compound quantity of the membrane is 30-70%, surface resistance is $0.01-5\Omega\cdot\text{cm}^2$, selective static migration constant of ion is 0.85-0.99, and folding angle is 0° .

25 3. A preparation method for the ion exchange membrane based on the microporous polypropylene film, characterized in that an one-step method and a two-step method may be applied in process route:

a. one-step method: mixing one or more kinds of monomer with ion-exchange group and other accessory ingredients to form a mixed solution, 30 dipping a microporous polypropylene film in the mixed solution, obtaining an

ion exchange membrane by polymerizing the monomers in the microporous film, and achieving finished product after washing;

b. two-step method: (1) mixing one or more kinds of monomer able to introduce ion exchange groups, and other accessory ingredients to form a mixed solution, dipping a microporous polypropylene film in the mixed solution, obtaining an original type composite membrane by polymerizing the monomers in the microporous film, obtaining an ion exchange membrane by introducing ion exchange groups into the original type composite membrane, and achieving finished product after washing.

4. The preparation method for the ion exchange membrane according to claim 3, characterized in that the monomers having or able to introduce ion exchange groups may be addition polymerization type or condensation polymerization type, and its polymerization reaction may be addition polymerization reaction or condensation polymerization reaction, and polymerization method comprises polymerization with initiator, polymerization initiated with thermo, polymerization initiated with UV ray or polymerization initiated with radiating of γ -ray.

5. The preparation method for the ion exchange membrane according to claim 3, 4, characterized in that the monomers having or able to introduce ion exchange groups may be selected from the group consisting of styrene, *p*-styrene sulfonate, chloromethyl styrene, *p*-aminostyrene, *p*-methylanino styrene, *p*-dimethylanino styrene, vinyl pridine, 2-methyl-5-vinyl pridine, acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, glycidyl acrylate, methylacrylic acid, glycidyl methylacrylate or mixtures thereof; said condensed type monomer having or able to introduce ion exchange groups may be selected from the group consisting of sulfocarboic acid, *p*-hyoxybenzylsulfonic acid, *o*-hydroxybenzoic acid, aniline, *m*-phenylenediamine, ethyleneciamine, diethylene triamine, tetraethylene peatamine, *p*-methyl phenylsulfonic acid, melamine, guanidine carbonate, dicyandiamide, ethyleneimine, dimethyl(4-hydroxybenzyl)amine, *m*-methyl

phenethylamine and formaldehyde, polyformaldehyde, ethanedial, furfuraldehyde and acetone, and the content of said monomers in the mixed solution is 30-100%.

6. The preparation method for the ion exchange membrane according to claim 3, characterized in that said accessory ingredients may be selected from initiator, cross-linking agent, flexibilizer, plasticizer, inorganic or organic solvent, wherein the initiator may be common azodiisobutyronitrile and benzoperoxide, and the content thereof in mixed solution is 0-5%; the cross-linking agent may be selected from the group consisting of divinylbenzene, butadiene, ethylene glycol dimethylacrylate, diethylene glycol dimethylacrylate, triethylene glycol dimethylacrylate, divinyl ether, phenol, cresol, resorcin, and the content thereof in mixed solution is 0-40%; the flexibilizer used in the present invention may be butadiene, styrene and the content thereof in mixed solution is 0-40%; the plasticizer may be dioctyl phthalate, dibutyl phthalate, and triphenyl phosphate, and the content thereof in mixed solution is 0-30%; the inorganic or organic solvent may be a common solvent such as water, carbon tetrachloride, ethylene tetrachloride or dichloroethane and the content thereof in mixed solution is 0-20%.

7. The preparation method for the ion exchange membrane according to claim 3, characterized in that the temperature and time for dipping the microporous polypropylene film in mixed solution is 0-50 °C and 0.1-24 hours, respectively.

8. The preparation method for the ion exchange membrane according to claim 3, characterized in that the dipped monomer is subjected to reaction at 50-100°C for 30 minutes to 24 hours.

9. The preparation method for the ion exchange membrane according to claim 3, characterized in that the method for introducing ion exchange groups may be selected from the group consisting of hydrolysis, sulfonation, or chloromethylation and aminization, wherein in the case of introducing an acidic ion exchange group by sulfonation, the sulfonating agent may be

selected from concentrated sulphuric acid, chlorosulfonic acid, sulfuric chloride, fuming sulfuric acid, sulfur trioxide and the temperature of sulfonation is 20-70°C.

- 5 10. The preparation method for the ion exchange membrane according to claim 3, characterized in that the membrane may be washed with acid, alkali, brine, organic solvent or water.

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